

We Claim:

1. A fluorochemical ester composition comprising:
one or more oligomers wherein each oligomer comprises (i) at least one fluorine-
containing repeatable unit and (ii) at least one fluorine-containing terminal group,
and wherein said compounds or oligomers comprise the condensation reaction
product of:

- (a) one or more fluorinated polyols;
- (b) one or more polyacyl compounds; and
- (c) one or more monofunctional fluorine-containing compounds
comprising a functional group that is reactive with the hydroxyl group of
said polyol (a) or with the acyl group of the polyacyl compounds (b).

2. The oligomers of claim 1 further comprising the reaction product of one or more
water-solubilizing compounds comprising one or more water solubilizing groups and at
least one electrophilic or nucleophilic moiety, said solubilizing groups independently
pendant from the repeating unit, or terminal portion.

3. The water solubilizing oligomers of claim 2 wherein said water-solubilizing group
is selected from the group consisting of carboxylate, sulfate, phosphate, sulfonate,
phosphonate, ammonium, and quaternary ammonium groups.

4. The oligomers of claim 1 further comprising the reaction product of one or more
polymerizable compounds comprising one or more polymerizable groups and at least one
electrophilic or nucleophilic moiety, said polymerizable groups independently pendant
from the repeating unit, or terminal portion.

5. The polymerizable oligomers of claim 4, wherein said polymerizable groups are
selected from the group consisting of acrylate, methacrylate, vinyl allyl, and glycidyl
groups.

6. The oligomers of claim 1 of the formula



wherein:

o is a number from 0 to 1 inclusive;

n is a number from 1 to 10 inclusive;

m is a number from 0 to 1 inclusive;

R_f is a perfluoroalkyl group having 1 to 12 carbon atoms, or a perfluoroheteroalkyl group having 3 to about 50 carbon atoms with all perfluorocarbon chains present having 1 to 6, preferably 1 to 4 carbon atoms;

Q is a divalent linking group;

R^1 is a polyvalent organic groups that is a residue of a polyacyl compound, that is a straight or branched chain alkylene, cycloalkylene, or heteroalkylene group of 1 to 14 carbon atoms; or an arylene of 6 to 12 carbon atoms;

R^2 is a divalent organic group that is a residue of the polyol, at least a portion of which are substituted with or contain one or more perfluoroalkyl groups, perfluoroheteroalkyl groups, perfluoroheteroalkylene groups, or mixtures thereof; and

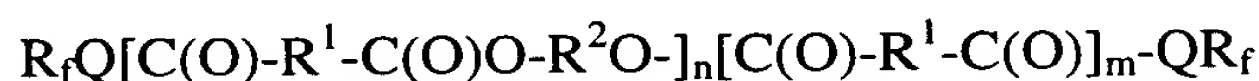
Z is R_fQ -, a water-solubilizing group, or a polymerizable group.

7. The oligomer of claim 6, wherein Q is selected from the following structures, wherein each k is independently an integer from 0 to about 20, R_1' is hydrogen, phenyl, or alkyl of 1 to about 4 carbon atoms, and R_2' is alkyl of 1 to about 20 carbon atoms:

$-\text{SO}_2\text{NR}_1'(\text{CH}_2)_k\text{O}(\text{O})\text{C}-$	$-\text{CONR}_1'(\text{CH}_2)_k\text{O}(\text{O})\text{C}-$
$-(\text{CH}_2)_k\text{O}(\text{O})\text{C}-$	$-\text{CH}_2\text{CH}(\text{OR}_2')\text{CH}_2\text{O}(\text{O})\text{C}-$
$-(\text{CH}_2)_k\text{C}(\text{O})\text{O}-$	$-(\text{CH}_2)_k\text{SC}(\text{O})-$
$-(\text{CH}_2)_k\text{O}(\text{CH}_2)_k\text{O}(\text{O})\text{C}-$	$-(\text{CH}_2)_k\text{S}(\text{CH}_2)_k\text{O}(\text{O})\text{C}-$
$-(\text{CH}_2)_k\text{SO}_2(\text{CH}_2)_k\text{O}(\text{O})\text{C}-$	$-(\text{CH}_2)_k\text{S}(\text{CH}_2)_k\text{OC}(\text{O})-$
$-(\text{CH}_2)_k\text{SO}_2\text{NR}_1'(\text{CH}_2)_k\text{O}(\text{O})\text{C}-$	$-(\text{CH}_2)_k\text{SO}_2-$
$-\text{SO}_2\text{NR}_1'(\text{CH}_2)_k\text{O}-$	$-\text{SO}_2\text{NR}_1'(\text{CH}_2)_k-$
$-(\text{CH}_2)_k\text{O}(\text{CH}_2)_k\text{C}(\text{O})\text{O}-$	$-(\text{CH}_2)_k\text{SO}_2\text{NR}_1'(\text{CH}_2)_k\text{C}(\text{O})\text{O}-$
$-(\text{CH}_2)_k\text{SO}_2(\text{CH}_2)_k\text{C}(\text{O})\text{O}-$	$-\text{CONR}_1'(\text{CH}_2)_k\text{C}(\text{O})\text{O}-$
$-(\text{CH}_2)_k\text{S}(\text{CH}_2)_k\text{C}(\text{O})\text{O}-$	$-\text{CH}_2\text{CH}(\text{OR}_2')\text{CH}_2\text{C}(\text{O})\text{O}-$
$-\text{SO}_2\text{NR}_1'(\text{CH}_2)_k\text{C}(\text{O})\text{O}-$	$-(\text{CH}_2)_k\text{O}-$

$-\text{C}_k\text{H}_{2k}-\text{OC}(\text{O})\text{NH}-$	$-\text{C}_k\text{H}_{2k}-\text{NR}_1'\text{C}(\text{O})\text{NH}-$,
$-\text{OC}(\text{O})\text{NR}'(\text{CH}_2)_k-$	$-(\text{CH}_2)_k\text{NR}_1'-$ and
$-(\text{CH}_2)_k\text{NR}_1'\text{C}(\text{O})\text{O}-$	

8. The oligomers of claim 1 of the formula



wherein:

5 n is a number from 1 to 10 inclusive;

m is 1;

R_f is a perfluoroalkyl group having 1 to 12 carbon atoms, or a perfluoroheteroalkyl group having 3 to about 50 carbon atoms with all perfluorocarbon chains present having 1 to 6, preferably 1 to 4 carbon atoms;

10 Q is a divalent linking group;

R^1 is a straight chain alkylene, of 1 to 14 carbon atoms;

R^2 is a polyvalent organic group which is a residue of the polyol, that is a straight or branched chain alkylene, cycloalkylene, arylene or heteroalkylene group of 1 to 14 carbon atoms, or an arylene group of 6 to 12 carbon atoms;

15 at least a portion of R^2 groups comprise one perfluoroalkyl group, perfluoroheteroalkyl group, perfluoroheteroalkylene group, or mixtures thereof.

9. The composition of claim 1 wherein the oligomer comprises the condensation reaction product of one or more fluorinated polyols, one or more non-fluorinated polyols, one or more polyacyl compound and one or more monofunctional fluorine-containing compounds.

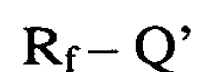
10. The composition of claim 1 wherein the oligomer comprises the condensation reaction product of one or more fluorinated polyols, an excess amount (relative to the polyol) of one or more linear alkylene diacyl compounds, and sufficient fluorinated monoalcohols to react with the terminal acyl groups

11. The fluorochemical composition of Claim 1 wherein the fluorine containing group of said polyol is a perfluoroalkyl group of 6 or fewer carbon atoms.

12. The fluorochemical composition of Claim 1 wherein the fluorine containing group of said polyol is a perfluoroalkyl group of 3 to 5 carbon atoms.

13. The fluorochemical composition of Claim 1 wherein the fluorine containing group of said polyol is a perfluoroalkyl group of is perfluorobutyl.

14. The fluorochemical composition of Claim 1 wherein the monofunctional fluorine-containing compound is a compound of the following formula I:



wherein:

R_f is selected from the group consisting of perfluoroalkyl group having 1 to 12 carbon atoms, and perfluoroheteroalkyl group having 3 to about 50 carbon atoms with all perfluorocarbon chains present having 6 or fewer carbon atoms;

Q' is a functional group that is reactive with the terminal acyl group of the polyacyl group or terminal hydroxy group of the polyol.

15. The monofunctional fluorine-containing compound of claim 14 wherein Q' is selected from hydroxyl, secondary amino, oxazoliny, oxazolonyl, acetyl, acetonyl, carboxyl, isocyanato, epoxy, aziridiny, thio, ester and acyl halide groups.

16. The fluorochemical composition of Claim 1 wherein said oligomers comprise the condensation reaction product of:

- (a) one or more fluorinated polyols;
- (b) one or more polyacyl compounds; and
- (c) one or more monofunctional fluorine-containing compounds comprising one functional group that is reactive with the hydroxyl group of said polyol (a) or with the acyl group of the polyacyl compound (b).

17. The fluorochemical composition of claim 16 wherein said fluorochemical oligomer further comprises the reaction product of one or more non-fluorinated polyols.

18. A coating composition comprising a mixture comprising:

- (a) a solvent and
- (b) the fluorochemical composition of Claim 1.

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19. The coating composition of claim 18 wherein said mixture comprises an aqueous solution, dispersion or suspension.

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20. The coating composition of claim 18 wherein the fluorochemical composition further comprises one or more water-solubilizing groups.

21. An article comprising a substrate having a coating of the fluorochemical composition of Claim 1 on one or more surfaces of said substrate.

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22. The article of Claim 21 wherein the fluorochemical composition further comprises one or more water-solubilizing groups.

23. The article of Claim 21 wherein the fluorochemical composition further comprises one or polymerizable groups.

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24. The article of Claim 21 wherein the substrate is selected from the group consisting of hard substrates and fibrous substrates.

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25. A method of imparting repellency to a substrate comprising the steps of :
applying the coating composition of claim 18 onto one or more surfaces of said substrate;
and curing the coating composition at ambient or elevated temperature.

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26. A polymer composition comprising:

- (a) the fluorochemical composition of claim 1; and
- (b) at least one thermoplastic or thermoset polymer.

27. The polymer composition of Claim 26 wherein said thermoplastic polymer is selected from the group consisting of polypropylene, polyethylene, polyacrylates, polymethacrylates, copolymers of ethylene and one or more alpha-olefins, polyesters, polyurethanes, polycarbonates, polyetherimides, polyimides, polyetherketones, polysulfones, polystyrenes, ABS copolymers, polyamides, fluoroplastics, and blends thereof; and said thermoset polymer is selected from the group consisting of polyurethanes, epoxy resins, fluoroelastomers, polyacrylates, polymethacrylates, and unsaturated polyesters, and blends thereof.

28. The polymer composition of Claim 26 wherein said composition is prepared by forming a melt blend of said fluorochemical composition and said thermoplastic polymer.

29. A shaped article comprising the polymer composition of claim 26, wherein said shaped article is selected from fibers, films, and molded articles.

30. A process for preparing shaped article comprising the steps of
(a) combining the fluorochemical composition of claim 1 and at least one thermoplastic polymer; and
(b) melt processing the resulting combination.